"Normal Aging" of Compounded Rubber

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK

By
HARLAN A. DEPEW, B.S., M.S.

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"Normal Aging" of Compounded Rubber[1,2]

Nine compounds were chosen for an investigation of "normal aging" under various conditions and after different times of storage. The report is divided into three parts: (I) aging of cured test slabs stored under different atmospheric conditions, including wet and dry; (II) aging of rubber under strain; (III) comparative aging of cured and uncured rubber. Tables and curve sheets selected from a large mass of data are given to illustrate how these nine rubber compounds age.

THE aging of rubber products is the net resultant of chemical reactions and changes of a physico-chemical nature.

It has long been recognized that conditions of storage have an important influence on the normal aging of rubber products. Rubber products stored in a warm place deteriorate more rapidly than when stored in a cold place, and it probably was recognition of this fact that led to the development of the Geer[3] accelerated-aging test, which accelerates aging solely by increasing the temperature during storage. Oxygen is also an important factor in the aging of rubber products. In normal storage the oxygen concentration varies very little, and depends only on the barometric pressure. In specific cases, such as inner tubes, the oxygen concentration may vary considerably according to the air pressure in the tube. Recognition of this as well as the temperature factor led to the development of the Bierer-Davis[4] oxygen-bomb method of accelerated aging.

Aging is also affected by moisture. Stringfield[5] has pointed out the importance of humidity in testing, Conover[6] and the author have made recommendations for controlling laboratory humidity, and Stevens[7] has shown that moisture improves the resistance to aging of certain stocks.

[1] Received November 23, 1927.

[2] Presented by Mr. Depew in partial fulfilment of the requirements for the degree of doctor of philosophy from Columbia University.

[3] Geer and Evans, *India Rubber J.*, **61**, 1163 (1921).

[4] Bierer and Davis, IND. ENG. CHEM., **16**, 711 (1924); **17**, 860 (1925).

[5] *Ibid.*, **17**, 833 (1925).

[6] Conover and Depew, *Proc. Am. Soc. Testing Materials*, **27**, 493 (1927).

[7] *J. Soc. Chem. Ind.*, **39**, 251T (1920).

It is well known that conditions of strain influence the life of vulcanized rubber and that light accentuates the deterioration. It seems probable that fluctuations in temperature and humidity, including freezing temperatures, may also affect the life of rubber products in storage. Consequently, there is no such thing as normal storage and statements giving the number of months' normal storage equivalent to one day's accelerated aging are meaningless unless the conditions of normal storage are carefully prescribed.

Consider the Geer test in its relation to "normal aging." The accelerated test is conducted at 70° C. If the "normal aging" is conducted at 20° C., the temperature difference is 50° C., enough to accelerate the aging 172 times on a basis of an increase of 2.8 times for each 10° C. On the other hand, with the storage temperature at 30° C. the acceleration of aging would be 61 times. In the former case an investigator would report one day of accelerated aging as approximately equivalent to 6 months' storage; in the latter, one day would be equivalent to 2 months' storage.

From these considerations one can readily understand why investigators are unable to agree on the quantitative relation between accelerated and "normal" aging tests. Inasmuch as conditions of accelerated aging can be controlled more easily than conditions of "normal aging" during the shorter time of test, accelerated tests can probably be duplicated more easily than natural aging tests. This alone justifies considerable interest in accelerated aging tests.

As a first step in the understanding of accelerated aging tests, a program was outlined to obtain information about "normal aging." Nine compounds were chosen (Table I) and the aging was determined after various conditions and times of storage.

I—Aging of Cured Test Slabs Stored under Different Atmospheric Conditions

The test slabs were 5 by 6 by 0.15 inch (12.7 by 15.2 by 0.38 cm.) in size and were suspended from a steel rod by paper clips in boxes maintained at the desired atmospheric conditions as follows:

(1) Outdoors on the roof of the laboratory in an open box protected from direct light by shutters. (Figure 1) The temperature varied from below zero (−17.8° C.) to over 100° F. (37.8° C.). The relative humidity varied from 40 per cent to 100 per cent. The average figures for the 4 years were 48° F. (8.9° C.) and 72 per cent relative humidity.

(2) Indoors in a duplicate open box in a dark room. The temperature varied from about 50° F. (10° C.) to 85° F. (29.4° C.) and the relative humidity varied from 25 per cent to 100 per cent. In the winter the average humidity was lower indoors than out, and in the summer the average indoor humidity was unusually high, owing to an air-washing installation in the building.

(3) Indoors in a tight box lined with sheet zinc. Air, dried

Table I—Compounds Investigated

(Figures in parts by weight)

Compound	Pale Crepe	Sulfur	Hexamethylenetetramine	XX Red Zinc Oxide	Clay	Paraffin	Triphenylguanidine	Magnesia	Black Label Kadox
A—Typical white tread stock	920	55	6	1260	...	..	..	..	..
B—Lower sulfur white tread stock	920	37	13	1260	...	..	..	..	..
C—Gum compound with zinc oxide for activation	920	55	6	28	...	..	..	..	..
D—"Pure gum" compound	920	55	..	..	...	..	..	..	..
E—Clay compound	920	55	6	..	597	..	..	..	..
F—Compound containing paraffin	920	55	6	1260	...	5	..	..	..
G—Compound with T. P. G. substituted for hexa	920	55	..	1260	...	..	12	..	..
H—Inorganic accelerated compound	920	55	..	1148	...	..	..	64	..
I—Compound containing a fine-particle-size zinc oxide	920	37	6	..	...	..	..	..	1035

1260 parts of zinc oxide by weight compared with 920 parts of rubber calculates as 22.5 volumes of pigment to 100 volumes of rubber.

by passing through sulfuric acid, was passed through the box continuously.

(4) Indoors in a tight box lined with sheet zinc. Air, humidified by bubbling through moist glass wool, was passed through the box continuously.

The effectiveness of the drying and humidification was demonstrated qualitatively by the fact that the iron clips holding the samples corroded through in the wet box in a short time, whereas there was practically no corrosion in the dry box.

Results and Discussion of Data—(1) The stress-strain curves made for slabs that had received 4 years of normal aging show that in most cases the rubber stored in the wet box has the "softest" stress-strain curve and rubber stored in the dry box has the "stiffest" stress-strain curve. (Curves 1 to 21)

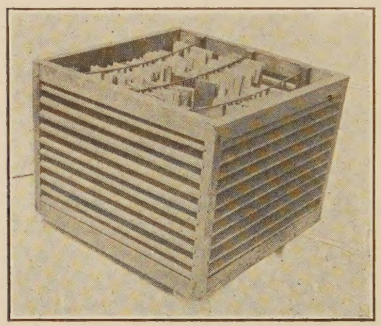


Figure 1—Arrangement of Test Slabs in the Open Storage Boxes; the Slabs Being Supported from Metal Rods by Clips. They Are Protected from Direct Light by Open Shutters and a Wooden Top

(2) Overcured rubber deteriorates faster in a dry than in a wet atmosphere; the reverse is the case for undercured rubber. (Curves 1 to 21 and 22 to 23) Stevens[7] showed that moisture improved the aging resistance of his stock. If the rubber compounds with which he experimented were tightly cured—and this seems probable—his results are in complete harmony with those of the present writers.

(3) The improvement in aging of the overcures in a wet atmosphere and of the undercures in a dry atmosphere is somewhat masked on the curve sheets by the superior aging that is shown by some of the compounds in the open box outdoors.

A possible explanation of this surprising fact is based on the belief of many technologists that rubber ages better in service than on the shelf. Changes in humidity with corresponding changes in moisture content, and therefore volume, and changes in temperature with resultant contraction and expansion, might work the rubber sufficiently to improve its resistance to aging. It is planned to check this theory by experimental tests. In the meantime it will serve until some better explanation is offered.

(4) The 60-minute cure of the clay compound (E) aged much better in the dry box than in the wet box. (Curves

13 and 14) Visual observation would have led to the opposite conclusion, for the surface of the slab aged in the dry box had hardened and could easily be cracked by bending. (Figure 2) Although the surface of the test slab in the dry box was poorer than that in the wet box, the center of the slab in the dry box appeared to be better than that in the wet box.

The fact that slabs of rubber only 1/8 inch (3 mm.) thick show a marked difference in aging on the surface and in the interior is especially interesting. The stress-strain curves of these test slabs are concave to the elongation axis. This is due to minute failures in the test piece (surface breaks) as it stretches. At first the surface carries most of the stress, but when the surface cracks the soft center has to carry the load. This concave curve can be noted in fiber compounds when the rubber-fiber bond breaks down, and in heavily loaded stocks when the rubber-pigment bond is breaking down.

The composition of the clay stock may not have been such as to give the best results obtainable with such a stock; therefore, no direct pigment comparison can be made or is intended. The stock aged poorly, doing best in the outdoors box.

The degree of surface cracking depends on the state of cure, the higher cures showing the more severe cracking. All the cures of compound D, and the two highest cures of compound C in the dry box cracked on bending, but these pieces were brittle throughout their thickness and not only on the surface.

Table II—Effect of One Month's Drying at Room Temperature on Stress-Strain Properties of Test Slabs Aged in a Wet Atmosphere
(Compound A)

Time of Cure at 141.5° C.	Tensile Strength		Elong.	Load at Elongation of:					
				150%		300%		450%	
Min.	*Kg./sq. cm.*	*Lbs./sq. in.*	*%*	*Kg./ sq. cm.*	*Lbs./ sq. in.*	*Kg./ sq. cm.*	*Lbs./ sq. in.*	*Kg./ sq. cm.*	*Lbs./ sq. in.*
AGED 4 YEARS AND 3 MONTHS IN WET BOX									
60	144	2055	545	23	320	53	750	105	1500
100	124	1765	475	32	455	66	945	119	1690
110	126	1795	480	32	460	62	875	118	1680
130	95	1355	385	36	505	67	945	Break	
AGED 4 YEARS AND 2 MONTHS IN WET BOX AND THEN 1 MONTH IN DRY BOX									
60	163	2320	540	28	395	65	920	121	1715
100	147	2095	475	39	555	83	1175	140	1985
110	122	1730	415	40	575	84	1195	Break	
130	113	1605	370	49	700	94	1330	Break	

(5) Slabs that have been aged for 4 years and 2 months in a wet box and then dried for 1 month by exposure to a dry atmosphere have a higher tensile strength by 300 to 400 pounds per square inch (21 to 28 kg. per sq. cm.) than slabs that have been kept continually in a wet atmosphere. Strangely enough, this improvement seems to be independent of state of cure. (Table II)

(6) During the first year's storage the change in weight

in the wet box is no doubt largely a measure of the change in moisture content. In all cases, except the "pure gum" compound, where the results were irregular, the slabs in the wet box gained the most in weight. The samples in the dry box actually lost weight in a number of cases. (Table III)

Figure 2—Strained Test Slab of Clay Compound (60-Minute Cure) after 4 Years in Dry Atmosphere

After the first year the rate of increase in weight in the wet box is less. It seems probable that the moisture content has reached equilibrium and that further changes in weight in both boxes are due largely to oxidation. The time required to come to equilibrium would probably have been greatly reduced if the dry or moist air had blown rapidly over the test slabs. In the indoors and outdoors boxes changes in temperature and humidity caused the weights to change irregularly.

Those data in Table III dealing with the change in weight of the slabs in the wet and dry boxes have been recalculated (Table IV) to show the difference in the increase in weight in the wet and dry atmospheres.

If the compounds oxidize at the same rate, the difference in weight increase should remain constant after the first year. If the test piece oxidizes more rapidly in the dry box, the difference in weight increase should diminish. The data show, in the case of compound A, that the curves other than the overcure oxidize at about the same rate in both the wet and dry atmospheres but the overcure oxidizes less in the wet atmosphere.

Since the undercure of compound A, for example, oxidized at about the same rate in the wet and dry atmospheres, but deteriorated in physical properties to a greater extent in the wet atmosphere as shown by tensile strength tests, it must be concluded that oxidation alone will not explain the aging of rubber. Without these data one might think that moisture in rubber influenced aging because it simultaneously influenced oxidation to a corresponding degree.

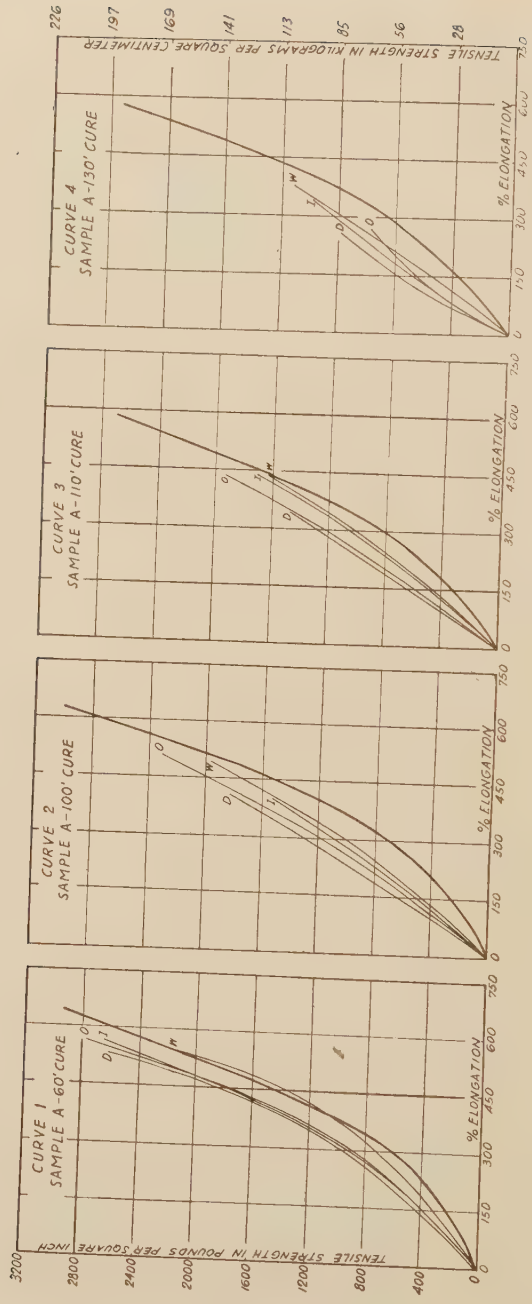
Boggs and Blake[8] have shown that the absorption of water causes rubber to swell. This swelling puts the rubber under continuous strain, which may cause it to age more rapidly from a physical viewpoint than would be expected from the

[8] Ind. Eng. Chem., 18, 224 (1926).

Table III—Change in Weight Calculated on a Basis of 100 Per Cent Rubber

(Figures in per cent)

Comp.	Time of Cure	Aged 4 Months				Aged 12 Months				Aged 24 Months				Aged 48 Months			
		Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box	Out-door	Indoor	Dry box	Wet box
A	60	+0 29	+0.22	−0.17	+0.37	+0.49	+0.20	−0.07	+1.73	+0.78	+0.20	+0.07	+1.88	−0.27	+0.27	+0.34	+2.05
	100	+0.32	+0.22	−0.10	+0.34	+0.63	+0.32	+0.24	+1.56	+1.12	+0.66	+0.54	+1.88	+0.59	+1.39	+0.98	+2.34
	110	+0 34	+0.24	−0.05	+0.41	+0.63	+0.39	+0.34	+1.83	+1.17	+0.81	+0.68	+2.02	+0.61	+1.46	+1.12	+2.54
	130	+0.41	+0.46	+0.07	+0.41	+0.90	+0.73	+0.59	+2.00	+1.78	+1.20	+1.10	+2.15	+1.46	+1.93	+2.09	+3.00
B	50	+0.41	+0.12	−0.29	+0.41	+0.44	+0.07	−0.29	+1.95	+0.44	+0.02	−0.10	+2.32	−0.12	+0.02	+0.22	+2.37
	80	+0.22	+0.02	+0.07	+0.46	+0.34	−0.07	−0.19	+2.57	+0.56	+0.07	+0.07	+2.20	−0.05	+0.48	+0.56	+2.52
	90	+0.22	+0.15	−0.24	+0.51	+0.29	+0.10	+0.07	+2.69	+0.46	+0.31	+0.82	+2.30	+0.22	+0.82	+1.62	+2.76
	120	+0.31	+0.31	+0.34	+0.65	+0.61	+0.65	+1.21	+3.00	+1.40	+1.45	+2.08	+2.93	+1.31	+2.45	+3.61	+3.87
C	50	+0.27	+0.15	−0.24	+0.31	+0.31	+0.15	−0.21	+1.49	+0.52	+0.27	−0.10	+1.52	0.0	+0.43	+0.24	+1.80
	90	+0.27	+0.24	0.0	+0.46	+0.58	+0.57	+0.37	+1.92	+1.71	+1.16	+0.72	+2.06	+2.11	+1.86	+1.34	+2.70
	100	+0.21	+0.28	−0.04	+0.60	+0.71	+0.72	+0.37	+2.37	+1.99	+1.37	+0.97	+2.43	+2.56	+2.18	+2.01	+3.05
	120	+0.57	+0.62	+0.09	+0.98	+1.71	+1.46	+0.63	+3.09	+2.98	+2.38	+1.59	+3.23	+4.12	+4.27	+3.52	+3.94
D	180	+0.37	+0.30	−0.05	+0.39	+0.48	+0.23	+0.05	+1.68	+0.74	+0.21	+0.14	+1.74	+0.90	+0.41	+0.62	+2.40
	240	+0.41	+0.30	+0.05	+0.43	+0.53	+0.30	+0.23	+1.90	+0.85	+0.42	+0.98	+1.79	+2.11	+1.18	+3.89	+2.66
	270	+0.39	+0.23	0.0	+0.39	+0.62	+0.32	+0.19	+2.16	+1.27	+0.84	+1.22	+2.27	+2.83	+2.32	....	+7.86
	330	+0.53	+0.33	0.0	+0.53	+1.28	+0.59	+0.23	+2.66	+3.33	+1.78	+2.06	+3.30	+4.85	+7.31	+3.92	+8.89
E	60	+0.29	+0.15	−0.12	+0.46	+0.74	+0.29	+0.19	+2.37	+1.39	+0.82	+1.40	+3.15	+1.81	+2.26	+2.63	+6.12
	90	+0.38	+0.17	−0.10	+0.58	+1.01	+0.55	+0.38	+3.11	+1.93	+1.39	+1.54	+5.47	+2.34	+3.40	+2.75	+8.74
	100	+0.38	+0.31	+0.03	+0.63	+1.11	+0.72	+0.65	+3.20	+1.95	+1.66	+2.38	+5.30	+2.29	+3.61	+3.23	+8.55
	130	+0.55	+0.53	+0.10	+0.72	+1.42	+1.23	+0.91	+3.59	+2.33	+2.98	+2.57	+6.77	+2.72	+4.00	+3.44	+8.89
F	50	+0.32	+0.15	−0.24	+0.27	+0.34	+0.12	−0.17	+1.22	+0.56	+0.12	−0.10	+1.39	+0.07	+0.15	+0.15	+1.56
	80	+0.29	+0.15	−0.15	+0.37	+0.39	+0.17	0.0	+1.46	+0.81	+0.29	+0.56	+1.59	+0.02	+0.41	+0.68	+1.80
	90	+0.29	+0.22	−0.17	+0.29	+0.46	+0.27	+0.02	+1.32	+0.95	+0.34	+0.39	+1.56	+0.54	+0.68	+0.71	+1.71
	120	+0 32	+0.32	−0.15	+0.32	+0.61	+0.49	+0.17	+1.68	+1.29	+0.93	+0.54	+1.83	+1.37	+1.58	+1.20	+2.20
G	70	+0.22	+0.05	−0.09	+0.19	+0.46	+0.41	+0.27	+1.10	+1.05	+1.05	+0.61	+1.24	+1.07	+1.73	+1.15	+1.65
	90	+0 22	+0.02	−0.12	+0.19	+0.51	+0.44	+0.51	+1.29	+1.14	+0.98	+0.98	+1.39	+1.39	+1.90	+2.00	+1.92
	100	+0.17	+0.07	+0.07	+0.22	+0.49	+0.56	+0.75	+1.29	+1.12	+1.27	+1.58	+1.49	+1.46	+2.41	+3.46	+2.21
	130	+0.32	+0.61	+0.15	+0.63	+0.90	+1.53	+1.22	+2.00	+1.83	+1.43	+2.65	+2.49	+2.26	+4.38	+4.87	+3.63
H	90	+0.38	+0.26	+0.05	+0.50	+0.79	+0.40	+0.14	+2.21	+1.33	+0.60	+0.38	+4.45	+0.55	+0.95	+0.74	+6.14
	150	+0.45	+0.43	+0.17	+0.55	+0.95	+0.74	+0.55	+2.26	+2.02	+1.07	+0.91	+4.19	+2.43	+1.83	+1.67	+6.81
	180	+0.50	+0.38	+0.29	+0.62	+1.33	+0.86	+0.83	+2.62	+2.91	+1.50	+1.40	+4.77	+3.72	+2.71	+3.07	+7.48
	210	+0.64	+0.62	+0.74	+0.76	+1.76	+1.33	+1.83	+4.17	+3.26	+2.53	+3.38	+6.59	+4.23	+4.52	+5.88	+9.60
I	30	+0.26	0.0	−0.13	+0.76	+0.22	....	....	+1.33	+0.26	....	....	+1.41	....	....	....	+1.41
	50	+0.39	+0.02	−0.20	+0.83	+0.52	....	....	+1.41	+0.76	....	....	+1.94	....	....	....	+1.74
	60	+0.43	+0.11	−0.30	+0.85	+0.72	....	....	+1.52	+1.11	....	....	+1.83	....	....	....	+2.09
	90	+0.63	+0.26	+0.15	+0.89	+1.15	....	....	+1.85	+2.13	....	+2.59	+2.44	....	....	....	+3.02


CURVE 1
SAMPLE A-60' CURE
CURVE 2
SAMPLE A-100' CURE
CURVE 3
SAMPLE A-110' CURE
CURVE 4
SAMPLE A-130' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
0
150
300
450
600
750
400
800
1200
1600
2000
2400
2800
3200
28
56
85
113
141
169
197
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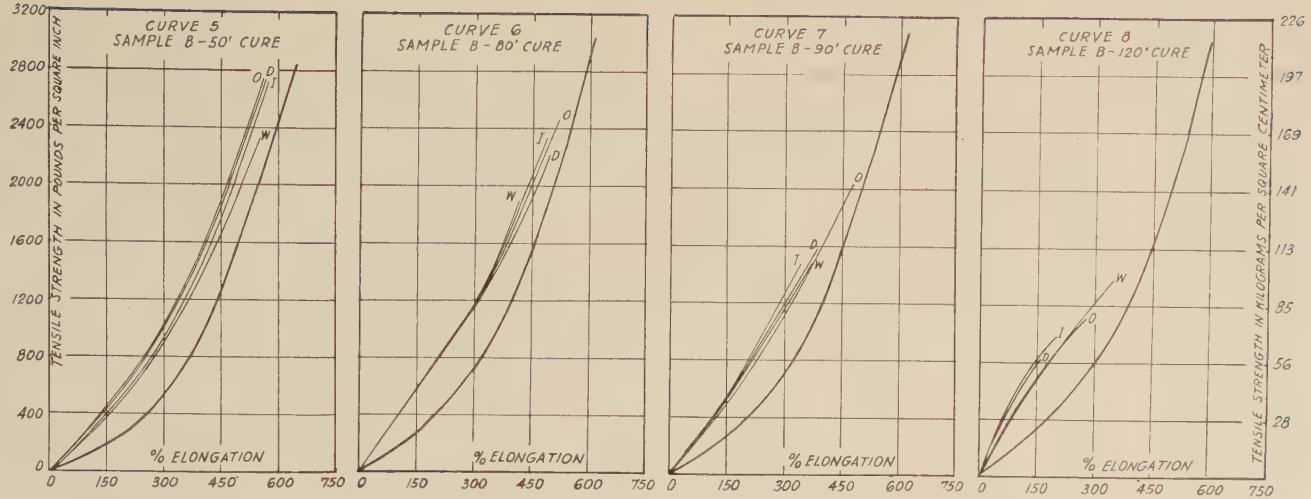


Note—In Curves 1 to 24 the heavy line shows stress-strain curve before aging. *W* is stress-strain curve obtained after 4 years' storage in a moist atmosphere; *D* is stress-strain curve obtained after 4 years' storage in a dry atmosphere; *I* is stress-strain curve obtained after 4 years' storage indoors; and *O* is stress-strain curve obtained after 4 years' storage outdoors.

data on the weight increase due to oxygen absorption; this difference in physical-chemical aging is especially large in undercured stocks, which swell to the greatest extent.

Since moisture retards the oxidation of an overcured slab, why does it not greatly reduce the oxidation of the undercured compound, where much more moisture is absorbed? The answer is probably linked closely with the structure of rubber.

Table IV—Difference in Weight Increase in Wet and Dry Atmospheres, Calculated on a Basis of 100 Parts of Rubber

(Figures in per cent)

Comp.	Time of Cure	Time of Aging—Months						
		4	8	12	18	24	36	48
	Min.							
A	60	0.54	1.15	1.80	1.81	1.81	1.64	1.71
	100	0.44	0.86	1.32	1.39	1.34	1.22	1.36
	110	0.46	0.85	1.49	1.44	1.34	1.24	1.42
	130	0.34	0.76	1.41	1.22	1.05	0.88	0.91
B	50	0.70	1.55	2.24	2.54	2.42	2.01	2.15
	80	0.39	1.84	2.76	2.41	2.13	2.74	1.96
	90	0.75	1.70	2.62	2.09	1.48	1.07	1.14
	120	0.31	0.92	1.79	1.25	0.85	0.43	0.26
C	50	0.55	1.16	1.70	1.65	1.62	1.21	1.56
	90	0.46	0.96	1.55	1.29	1.34	1.14	1.36
	100	0.64	1.32	2.00	1.65	1.46	1.06	1.04
	120	0.89	1.79	2.46	2.01	1.64	0.70	0.42
D	180	0.44	1.18	1.63	1.75	1.60	1.29	1.78
	240	0.38	0.97	1.67	1.44	0.81	−0.87	−1.23
	270	0.39	1.27	1.97	1.71	1.02	..	..
	330	0.53	1.59	2.43	2.09	1.24	2.32	4.97
E	60	0.58	1.35	2.18	2.20	1.75	2.13	3.49
	90	0.68	1.63	2.73	3.14	3.93	5.34	5.99
	100	0.60	1.45	2.55	2.77	2.92	4.83	5.32
	130	0.62	1.59	2.68	2.85	4.20	4.99	5.45
F	50	0.51	0.96	1.39	1.90	1.49	1.42	1.41
	80	0.52	0.97	1.46	1.41	1.03	1.10	1.12
	90	0.46	0.90	1.30	1.39	1.27	1.07	1.00
	120	0.47	0.88	1.51	1.42	1.29	1.05	1.00
G	70	0.38	0.69	0.83	0.73	0.63	0.49	0.50
	90	0.31	0.49	0.78	0.52	0.41	0.21	−0.08
	100	0.15	0.22	0.54	0.22	−0.09	−0.54	−1.25
	130	0.48	0.61	0.78	0.17	−0.16	−0.61	−1.24
H	90	0.45	1.26	2.07	3.31	4.07	4.59	5.40
	150	0.38	1.07	1.71	2.47	3.28	4.43	5.14
	180	0.33	1.00	1.79	2.55	3.37	4.10	4.41
	210	0.02	1.30	2.34	2.95	3.21	3.60	3.72
I	30	0.89	1.35	..	..	..	..	..
	50	1.03	1.48	..	..	..	..	..
	60	1.15	1.65	..	..	..	..	..
	90	0.74	0.95	..	..	..	..	..

Compounds B, C, and F behaved similarly to A. In the case of D the results were erratic. Moisture was more effective in reducing oxidation in compound G than any other, and the physical results for this compound were especially good in the wet atmosphere. The large increases in weight of E and H in the wet atmosphere year after year were probably due to hydration of the clay and magnesia.

(7) The change in weight of the rubber slabs in the dry box proved to be a good criterion of the deterioration during aging (Curve 24 and Table V). This conclusion would

be less reliable where moisture was present, because of the influence of varying amounts of hygroscopic material.

When the test slabs in the dry box have increased 1 per cent in weight calculated on the rubber in the compound, they have lost about 50 per cent of their reënforcing properties, and they continue to lose about 50 per cent for each increase of 1 per cent in weight.

II—Aging of Rubber under Strain

Light has a decided deteriorating effect on rubber under strain. Even light that has passed through a window pane, which cuts out the shorter wave lengths, causes cracking.

Since this kind of aging is believed to be different from aging "on the shelf," tensile test pieces of each cure were fastened to boards under initial strains of 50 and 200 per cent elongation, and one of the sets of test pieces was placed on the roof in the sunlight and the other in the dark in a loft over the laboratory.

The test pieces that were exposed to the sun and weather showed a considerable variation in resistance to light. Compound D, which contained no pigment, failed within a few hours and the opening of the cracks could be watched. Compound C, with only zinc oxide for activation, showed slightly greater resistance to the light, and the other compounds showed a marked superiority, especially compound F which contained paraffin. The value of paraffin in this respect is well recognized by rubber technologists.

Qualitative observations with the non-pigmented compound (D) showed that the destruction was especially rapid on a hazy day—this may be attributed to humidity. It seems probable that accelerated aging tests where the rubber compounds have been exposed to light have not given sufficient attention to the moisture content of the rubber and the atmosphere. At the end of about $1^1/_2$ years all the samples except a few of F compound had broken or had assumed a set so high that the stress had become practically zero. The exact number of days for each piece to break is given in Table VI.

The samples were left in this condition for 4 years and 10 months, when the test pieces that had not failed were tested for tensile properties. The results of the tests are given in Table VII. The surface of these test pieces was checked and a chalky layer 0.01 inch (0.25 mm.) deep was found. The cross section of the solid center of the test piece that had been stretched to 200 per cent elongation was about 0.08 by 0.04 inch (2.03 by 1.02 mm.). A tensile force of $2^2/_3$ pounds (1.2 kg.) was required to break it, which calculates to 835 pounds per square inch (59 kg. per sq. cm.). This is a remarkable figure considering the aging exposure

Table V—Relation of Change in Weight to Decrease in Area under Stress-Strain Curve of Test Pieces Stored in a Dry Atmosphere

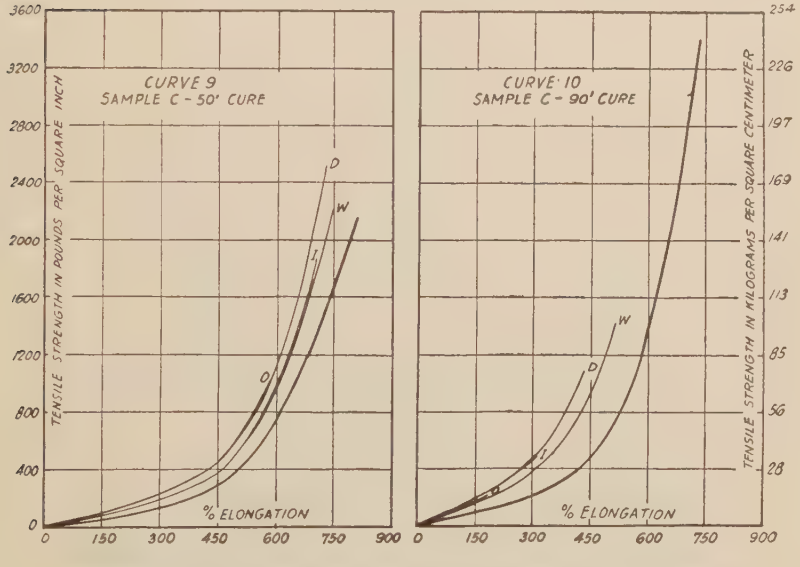
Cure	After 2 Years' Aging									After 4 Years' Aging								
	A	B	C	D	E	F	G	H	I	A	B	C	D	E	F	G	H	I
	Per cent decrease in area under stress-strain curve																	
Under	8	−12	−10	9	35	−16	−10	−4	−36	7	−13	−25	46	68	−40	4	−7	−40
Intermediate	29	5	52	71	64	3	44	41	17	40	20	66	98	80	8	78	68	−3
Intermediate	43	33	72	90	70	23	69	63	10	51	47	93	99	89	32	86	71	13
Over	61	68	96	98	86	58	81	81	70	63	87	99	99	94	66	86	93	89
	Per cent increase in weight calculated on basis of 100% rubber																	
Under	0.07	−0.10	−0.10	0.14	1.40	−0.10	0.61	0.38	..	0.34	0.22	0.24	0.62	2.63	0.15	1.15	0.74	..
Intermediate	0.54	0.07	0.72	0.98	1.54	0.56	0.98	0.91	..	0.98	0.56	1.34	3.89	2.75	0.68	2.00	1.67	..
Intermediate	0.68	0.82	0.97	1.22	2.38	0.29	1.58	1.40	..	1.12	1.62	2.01	..	3.23	0.71	3.46	3.07	..
Over	1.10	2.08	1.59	2.06	2.57	0.54	2.65	3.38	2.59	2.09	3.61	3.52	3.92	3.44	1.20	4.87	5.88	..

and speaks well for the protection afforded by the white pigment and the paraffin.

Tener, Smith, and Holt[9] have stated that dark-colored compounds are more resistant to sunlight than light-colored compounds. However, they used whiting in their work, whereas the writers used zinc oxide.

Stutz[10] has shown that there is a considerable difference in the opacity of these pigments to the short wave lengths of light, zinc oxide being entirely opaque at the shorter wave lengths whereas whiting is quite transparent. He has also shown that zinc oxide protects a paint film against chalking while pigments that are transparent at the shorter wave lengths fail to protect.

The protection given to rubber by zinc oxide is the same as that given to a paint vehicle. The color of the rubber compound in itself is of secondary importance in resistance to


CURVE 9
SAMPLE C - 50' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
% ELONGATION
CURVE 10
SAMPLE C - 90' CURE
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION

sunlight. The important factor is the opacity of the pigment to the particular wave lengths of light that are injurious.

Jecusco[11] has made a good start along this line in studying the deterioration of rubber caused by light through investigating the aging effect of different wave lengths.

This kind of deterioration has been a much more important problem to the paint chemist than to the rubber chemist, as the paint chemist is largely interested in surfaces. He has done a great deal of work on accelerated tests and we can profit by studying some of his methods.[12]

[9] *Bur. Standards, Tech. Paper* **342.**

[10] *J. Franklin Inst.*, **200**, 87 (1925).

[11] Ind. Eng. Chem., **18**, 426 (1926).

[12] Nelson and Schmutz, *Ibid.*, **18**, 1222 (1926).

Only a few test pieces which were exposed in the dark were broken after $3^1/_2$ years. Those that did break were the ones that had been given an initial strain of 200 per cent elongation.

Table VI—Days Required for Failure of a Test Piece Exposed to Weather under Strain

Comp.	50% Elongation				200% Elongation			
A	*60*[a]	*100*	*110*	*130*	*60*	*100*	*110*	*130*
	265	308	288	255	260	219	216	219
	274	344	294	304	265	222	211	224
	353	275	285	264	255	221	211	224
B	*50*	*80*	*90*	*120*	*50*	*80*	*90*	*120*
	285	275	304	241	236	224	225	217
	353	501	281	304	239	217	227	212
	366	285	305	229	243	231	219	214
C	*50*	*90*	*100*	*120*	*50*	*90*	*100*	*120*
	...	...	...	299	213	80(?)	65(?)	73(?
	...	...	...	...	209	37	41	67
	...	...	...	245	229	4	4	1
D	*180*	*240*	*270*	*330*	*180*	*240*	*270*	*330*
	...	...	...	...	221	31	37	1
	...	...	...	...	221	265	2	1
	...	...	602	635	265	1	1	1
E	*60*	*90*	*100*	*130*	*60*	*90*	*100*	*130*
	...	658	391	635	230	210	211	351
	740	...	...	314	338	215	198	...
	...	...	635	...	224	229	212	203
F	*50*	*80*	*90*	*120*	*50*	*80*	*90*	*120*
	...	...	...	...	...	...	602	217
	...	...	...	...	.	366	358	211
	...	...	...	.	.	635	602	212
G	*70*	*90*	*100*	*130*	*70*	*90*	*100*	*130*
	233	635	286	258	222	208	208	206
	305	339	635	262	224	209	209	200
	314	635	305	286	210	209	207	205
H	*90*	*150*	*180*	*210*	*90*	*150*	*180*	*210*
	740	...	789	...	224	184	198	49
	...	...	...	...	246	198	67	43
	...	602	...	...	238	200	200	31
I	*30*	*50*	*60*	*90*	*30*	*50*	*60*	*90*
	501	662	539	323	239	227	214	198
	635	662	635	391	232	231	205	200
	635	501	635	398	538	228	209	200

[a] Numbers in italics refer to minutes' cure at 40 pounds.

Whereas in sunlight overcures checked more rapidly than undercures, in the dark the reverse was the case. This was only a surface effect, however, and after $3^1/_2$ years of strain the undercures generally tested stronger than the overcures.

The distance between the marks on the tensile-strength test pieces, which were originally 3.81 cm. (1.5 inches) and 7.62 cm. (3 inches) in the stressed position, increased as time went on. Owing to the greater strain in the thin section of the test piece, this part weakened more than the thicker ends and in turn stretched further. The set on release was accordingly in many cases greater than the original amount of elongation.

III—Comparative Aging of Cured and Uncured Rubber

The uncured stock left after making the slabs required in the preceding part of this work was wrapped in holland cloth and

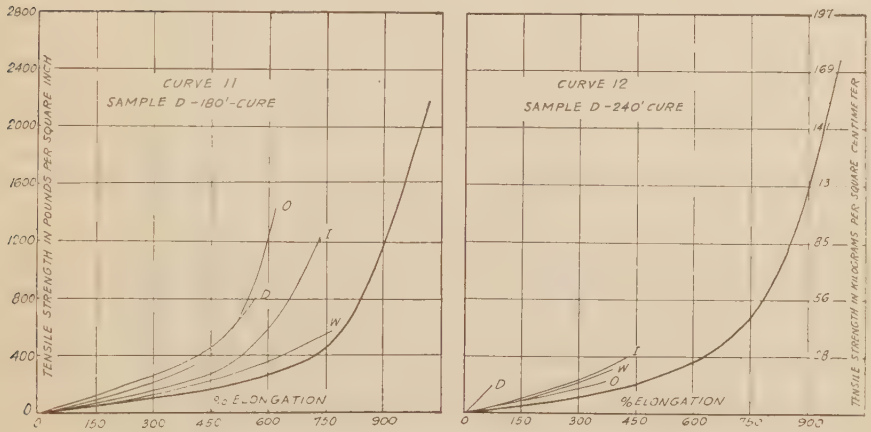
stored in a dark room in the laboratory for 18 and 36 months before curing.

The results of this storage are given in Table VIII. On comparing tests made on slabs cured up at the time of milling with similar stocks stored in the uncured state for 18 and 36 months and then cured, the following facts are noted:

(1) The optimum for the samples cured and tested 24 and 48 hours after milling was generally one of the two intermediate cures.

(2) After aging in the cured state the optimum came at the shortest cure, which is in line with the statement of Geer and Evans[3] that overcuring is a major factor in aging.

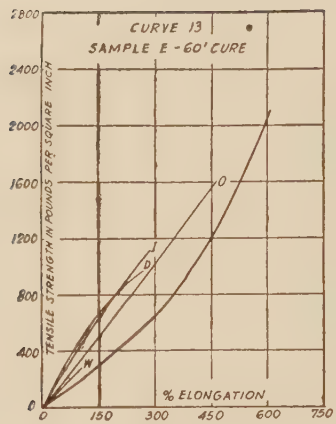
(3) The optimum in the case of the stock stored uncured occurred at the longest cure; the very reverse to the situation for storage in the cured state. Storage has retarded the cure.

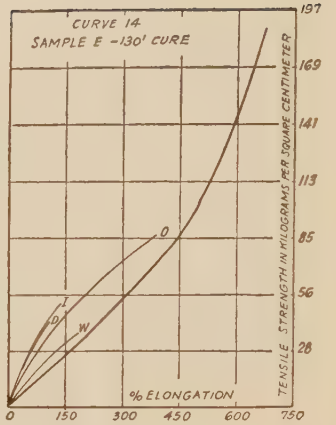


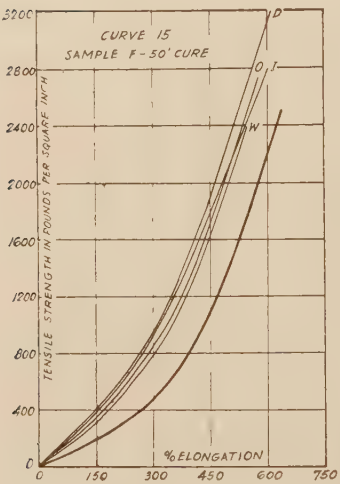
One of the stocks (G) deteriorated very appreciably in the uncured state. The reason for this peculiar behavior is an open question, but it has been generally observed that master batches of crude rubber with certain accelerators become very soft and sticky in a short time.

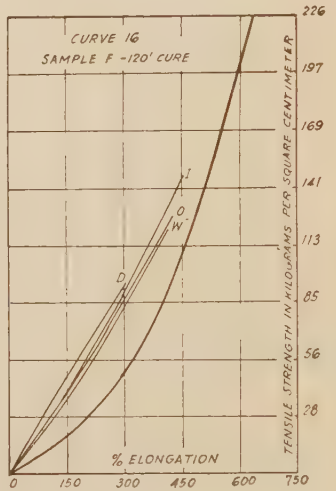
The most probable cause for the retardation in cure is the formation of sulfurous and sulfuric acid due to the oxidation of some of the sulfur in the compound. A second possibility is that the organic accelerator decomposes during storage. The fact that this retardation occurred in the case of compounds D and H, which contain no added organic accelerator, is partial negative evidence in favor of the first explanation.

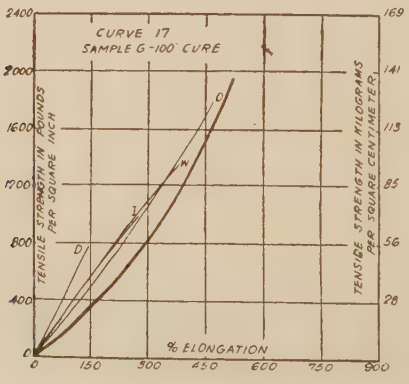
Some clay and carbon black stocks show a rapid retardation that has been attributed to adsorption of the accelerator by the pigment. Since the retardation is pronounced in the case of C, which contains practically no pigment, the adsorption explanation does not apply in this case.


CURVE 13
SAMPLE E - 60' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
% ELONGATION
D
O
W


CURVE 14
SAMPLE E - 130' CURE
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
I
D
O
W


CURVE 15
SAMPLE F - 50' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
% ELONGATION
D
O
I
W


CURVE 16
SAMPLE F - 120' CURE
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
I
O
W
D


CURVE 17
SAMPLE G - 100' CURE
TENSILE STRENGTH IN POUNDS PER SQUARE INCH
TENSILE STRENGTH IN KILOGRAMS PER SQUARE CENTIMETER
% ELONGATION
O
W
I
D

The extent of the retardation during the first 18 months is much greater than during the second 18 months.

The retardation of cure on storage of the uncured stock makes the practice of aging stocks for two or more weeks between milling and processing rather questionable. Certainly, if this is done it will be quite advantageous to keep this period constant.

Table VII—Physical Properties after Straining Test Pieces in Light for 4 Years and 10 Months

Sample	Time of Cure at 141.5° C.	Set	Thickness after Release of Tension		Load at Break	Tensile Strength[a]		Elongation at Break[b]
			Shoulder of tensile	Middle of tensile				
	Min.	%	*Cm.*	*Cm.*	*Kg.*	*Kg./sq. cm.*	*Lbs./sq. in.*	%
			STRETCHED 50 PER CENT					
F	50	85	0.384	0.312	4.4	18	255	460
	80	87	0.368	0.277	3.5	15	210	345
	90	87	0.351	0.251	3.0	13	190	280
	120	85	0.353	0.269	3.5	15	220	185
			STRETCHED 200 PER CENT					
F	50	235	0.366	0.183	1.2	5	70	400
	80	...	...	...	...	..	...	..
	90	...	...	...	...	..	...	...
	120	...	...	...	...	..	...	..

[a] Based on initial width and thickness.
[b] Based on marks originally 2.54 cm. apart.

It is also important to know whether the reënforcing properties have been affected by storage of the uncured stock. If not, it should be possible to bring the uncured stock back to practically its initial condition by adding organic accelerator.

The data in Table IX show that, although the initial properties can be nearly restored by this method, the stiffness of the stock especially at the higher cures, is greater, and the percentage elongation at break is less. It was also noted that the aged compound was sticky, and the added accelerator had to be milled in at low temperatures to prevent the stock from sticking to the back roll of the mill.

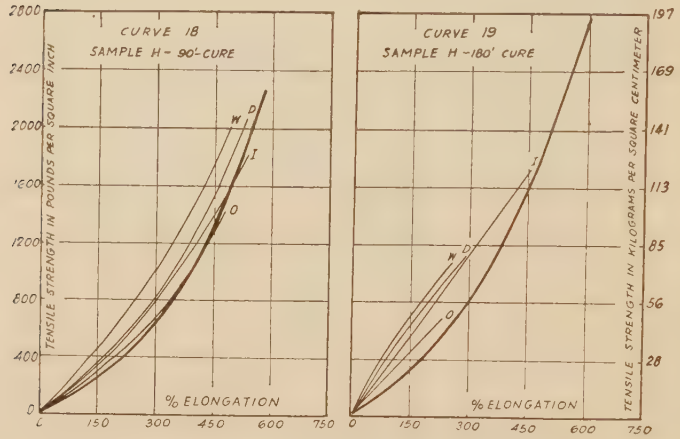
In the writers' opinion the deterioration in physical properties, though important, is secondary to the retardation of cure.

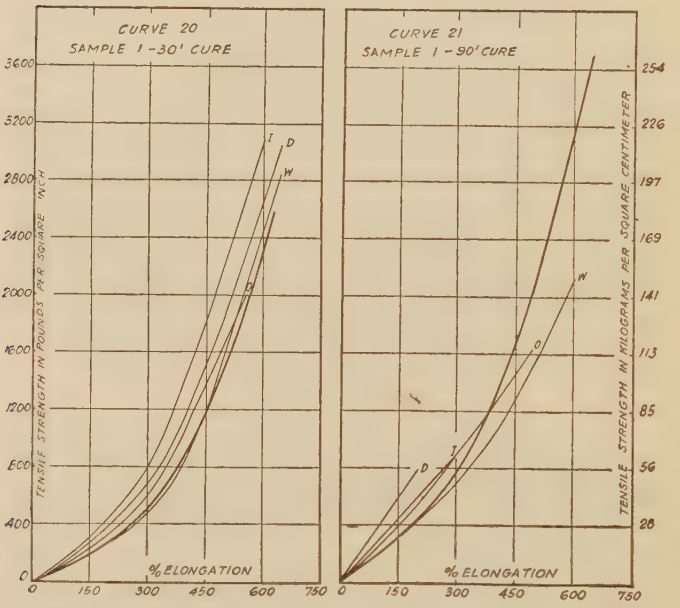
Conclusions

Part I—Compounded cured rubber stored in a wet box has a softer stress-strain curve than when stored in a dry box. If dried after a long exposure to a moist atmosphere the tensile strengths increase by 21 to 28 kg. per sq. cm. (300 to 400 pounds per square inch).

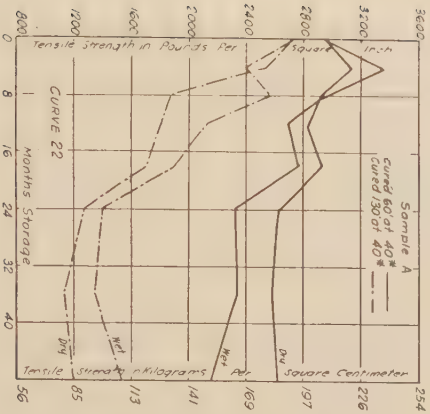
On a basis of tensile tests, overcured rubber deteriorates faster in a dry atmosphere than in a wet atmosphere and the reverse is the case for undercures. An undercure will oxidize at about the same rate in a wet as in a dry atmosphere, but an overcure will oxidize more rapidly in the dry atmosphere as shown by changes in weight.

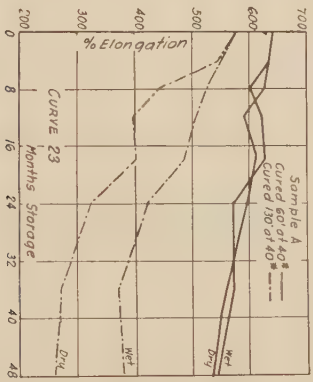
The change in weight of samples stored in a dry box, which excludes moisture changes, proved a good criterion of their deterioration. Each increase of 1 per cent in weight calculated on the rubber content showed a corresponding decrease in reënforcing properties of 50 per cent.





PART II—The ability of zinc oxide and paraffin to protect rubber under strain against sunlight was shown and it was suggested that humidity was a factor. The protection that pigments offer against sun-cracking is the same in both paint


Tensile Strength in Pounds Per Square Inch
Tensile Strength in Kilograms Per Square Centimeter
CURVE 22
Months Storage
Sample A
Cured 60° at 40#
Cured 130° at 40#
Wet
Dry


% Elongation
CURVE 23
Months Storage
Sample A
Cured 60° at 40#
Cured 130° at 40#
Wet
Dry

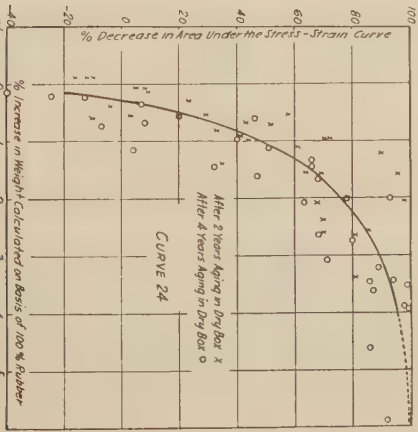

% Decrease in Area Under the Stress-Strain Curve
% Increase in Weight Calculated on Basis of 100% Rubber
CURVE 24
After 2 Years Aging in Dry Box x
After 4 Years Aging in Dry Box o

Table VIII—Relative Aging of Cured and Uncured Compounds

Comp.	Time Cure at 40 Lbs.	Original			After 18 Months' Aging Indoors						After 36 Months' Aging					
					Cured			Uncured			Cured			Uncured		
		Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.	Tensile strength	Elong.	Load at 300% elong.
	Min.	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*
A	60	2940	640	615	3100	640	595	2165	590	505	2655	565	775	2150	595	610
	100	3020	630	730	2485	575	960	2910	620	685	1905	455	1090	2435	585	785
	110	2715	585	815	2370	530	1000	2945	610	720	1920	475	1050	2415	565	760
	130	2725	575	865	1915	475	1050	3125	610	785	1460	355	1215	2530	590	825
B	50	2830	650	495	3090	620	760	1770	570	470	2675	580	815	1505	560	495
	80	3040	610	705	2490	530	1000	2845	630	600	2285	485	1140	2215	575	760
	90	3095	620	675	2370	525	1045	2845	605	710	1910	430	1130	2135	570	705
	120	3050	590	800	1375	350	1195	3085	605	765	855	215	..	2295	590	655
C	50	2155	805	140	2185	780	155	1330	830	90	1450	690	135	1000	840	75
	90	3400	730	220	2050	600	300	1535	710	145	610	415	345	2110	775	185
	100	3165	735	260	1865	555	365	2325	735	190	435	370	290	1850	735	180
	120	3135	685	305	265	195	..	2280	735	135	335	260	..	2765	740	230
D	180	2165	1020	100	2020	1000	100	1750	990	...	1840	855	160	Stock lost		
	240	2470	980	120	1590	760	100	2025	985	35	1470	760	180			
	270	2800	945	130	1785	835	90	540	890	85	190	410	220			
	330	2425	890	150	275	490	125	1155	880	95	245	120	..			
E	60	2115	610	660	2175	590	840	1705	575	540	1610	435	1170	1670	480	810
	90	2210	635	680	1865	540	990	2145	635	710	1000	245	..	2105	535	980
	100	2175	650	715	1670	510	935	2325	685	700	890	195	..	2230	560	985
	130	2650	670	795	1290	370	1095	2535	670	815	710	160	..	2460	595	1000
F	50	2500	635	455	2615	605	655	900	485	310	2765	580	825	1595	600	300
	80	2880	630	645	3005	610	820	2040	580	505	2645	560	770	1975	580	570
	90	3180	635	675	3135	615	930	2250	595	470	2430	550	1020	2130	585	680
	120	3190	635	700	2835	595	745	2595	620	655	2035	480	1075	2150	565	615
G	70	1645	530	640	1520	535	645	[a]			1160	435	830	[a]		
	90	2075	560	720	1395	440	865				1150	345	1030			
	100	1955	520	810	1630	460	980				1040	295	..			
	130	1475	420	1085	900	250	..				765	170	..			
H	90	2260	580	625	2435	635	580	1735	535	605	1700	510	660	1355	525	470
	150	2690	640	655	2665	595	825	2130	560	730	1745	475	895	1710	525	680
	180	2765	600	820	2335	570	925	2270	550	820	1875	460	980	1935	525	775
	210	2380	600	795	1375	435	980	2335	580	840	700	170	..	2085	560	750
I	30	2580	625	470	3200	590	700	1370	515	345	2985	605	715	1510	595	185
	50	3440	645	625	3050	595	730	1960	555	500	3060	605	730	2305	630	300
	60	3495	630	740	2780	545	960	2265	540	695	2405	505	1000	2465	610	490
	90	3690	645	770	2090	475	990	2565	600	680	1615	460	1030	2900	650	540

[a] The aged uncured stock was very tacky, stuck to cloth, and cured porous.

Table IX—Effect of Adding Accelerator to Aged Uncured Rubber

When Cured	Compound A				Compound C			
	Time of cure at 40 lbs.	Tensile strength	Elong.	Load at 300% elong.	Time of cure at 40 lbs.	Tensile strength	Elong.	Load at 300% elong.
	Min.	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*	*Min.*	*Lbs./sq. in.*	*%*	*Lbs./sq. in.*
Directly after mixing	60	2940	640	615	50	2155	805	140
	100	3020	630	730	90	3400	730	220
	110	2715	585	815	100	3165	735	260
	130	2725	575	865	120	3135	685	305
After 67 months' storage uncured	60	2130	560	655	50	1440	885	115
	100	2300	530	890	90	2440	775	150
	110	2520	550	910	100	2500	745	160
	130	2385	535	930	120	2620	715	230
After 67 months' storage uncured with the addition of 0.16% hexa calculated on rubber (1/4 original amount added)	60	2020	555	660	50	1820	890	80
	100	2520	545	970	90	2680	760	195
	110	2495	535	1000	100	2890	735	240
	130	2350	515	1100	120	3140	730	245
After 67 months' storage uncured with the addition of 0.32% hexa calculated on rubber	60	2460	600	660	50	2100	815	115
	100	2620	560	945	90	2700	655	275
	110	2610	555	970	100	3160	680	310
	130	2500	525	1085	120	2560	620	370
After 67 months' storage uncured with the addition of 0.65% hexa calculated on rubber	60	2545	585	755	50	2230	805	155
	100	2880	550	1045	90	2640	655	280
	110	2880	535	1140	100	3240	665	340
	130	2710	515	1230	120	2320	595	420

and rubber, and the large amount of work done by the paint chemist should be studied by the rubber technologist.

Part III—The effect of aging unvulcanized compounded rubber is to retard the cure greatly and to lower the reënforcing properties slightly. Unvulcanized compounded rubber that has lain around in holland cloth for several years is sticky and has to be milled on cold rolls, but after adding accelerator and vulcanizing a good product is obtained. The retardation, in this program, is not due to adsorption of accelerator by the pigment since some of these stocks are practically "pure gum" stocks.

If this program on "normal aging" were being started today, all of these nine compounds would not have been chosen; other formulas would have been used containing antioxidants that were unknown six years ago; certain new accelerators would have been used; and hygroscopic[6] reclaim stocks would have been added.

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VITA

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